

草珊瑚中一个新的苯基丙二醇类化合物*

段莹辉^{1,2}, 李 畅³, 戴 毅^{1,4}, 姚新生^{1,3,4**}

(1 暨南大学中药及天然药物研究所, 广东 广州 510632; 2 暨南大学中医博士后流动站, 广东 广州 510632; 3 沈阳药科大学中药学院, 辽宁 沈阳 110016; 4 广东省中药药效物质基础及创新药物研究重点实验室, 广东 广州 510632)

摘要: 从金粟兰科植物草珊瑚 (*Sarcandra glabra*) 全株的水提取物中分离得到一个新的苯基丙二醇类化合物 (2S)-3, 3-二-(4-羟基-3-甲氧基苯基)-丙-1, 2-二醇 (**1**), 以及一个已知化合物, 银线草内酯 E (**2**), 并利用 NMR、MS、旋光值等波谱学技术鉴定了其结构。

关键词: 草珊瑚; 金粟兰科; 苯基丙二醇

中图分类号: Q 946

文献标识码: A

文章编号: 2095-0845(2012)02-208-03

A New Phenylpropanediol from *Sarcandra glabra* (Chloranthaceae)DUAN Ying-Hui^{1,2}, LI Chang³, DAI Yi^{1,4}, YAO Xin-Sheng^{1,3,4**}

(1 Institute of Traditional Chinese Medicine and Natural Products, Jinan University, Guangzhou 510632, China; 2 Integrated Traditional Chinese and Western Medicine Postdoctoral Station, Jinan University, Guangzhou 510632, China; 3 School of Traditional Materia Medica, Shenyang Pharmaceutical University, Shenyang 110016, China; 4 Guangdong Province Key Laboratory of Pharmacodynamic Constituents of TCM and New Drugs Research, Jinan University, Guangzhou 510632, China)

Abstract: A new phenylpropanediol, (2S)-3, 3-di-(4-hydroxy-3-methoxyphenyl)-propane-1, 2-diol (**1**), along with a known compound, shizukanolide E (**2**) were isolated from the water extract of the whole plants of *Sarcandra glabra*. The structure was elucidated on the basis of extensive NMR, MS, and ORD spectral analysis.

Key words: *Sarcandra glabra*; Chloranthaceae; Phenylpropanediol

Sarcandra glabra (Thunb.) Nakai (Chloranthaceae), widely distributed in southern parts of China and southeast Asian, is an important traditional Chinese medicine used for antibacterial, antitumor and anti-inflammation effects (Takeda *et al.*, 1993). Previous phytochemical investigations on this plant reported the isolation of flavonoids, sesquiterpenes, triterpenoids, coumarins, and other phenolics (Hu *et al.*, 2009; Li *et al.*, 2006; Tsui and Brown, 1996; Takeda *et al.*, 1993; Huang *et al.*, 2010). The marketed products related to *Sarcandra glabra* such as Fufang Caoshanhu Hanpian, Qingre Xiaoyanning

Jiaonang, were extracted with water, so a phytochemical investigation on the water extract was necessary. In our continuation studies on this medicinal plant, a new compound (**1**) and a known compound (**2**) were isolated. Herein, we reported the isolation and structure identification of this new compound.

Results and discussion

Compound **1** was obtained as white amorphous powder, $[\alpha]_D^{25.8} +20.0$ (c. 0.9, CH₃OH). Its molecular formula was established as C₁₇H₂₀O₆ by HR-ESI-MS at m/z 319.1183 [M-H]⁻ (calcd for C₁₇

* Foundation items: Chinese Pharmacopeia Commission (TS-61) and Guangdong Technology Significant Project (2004Z1-E5011)

** Author for correspondence; E-mail: tyaoxs@jnu.edu.cn

Received date: 2011-11-10, Accepted date: 2012-02-01

作者简介: 段莹辉 (1983-) 男, 博士, 主要从事中药及天然药物活性成分研究。

H_{19}O_6 , 319.1182), indicating eight degrees of unsaturation. The IR spectrum displayed absorption bands for hydroxy groups ($3\,391\text{ cm}^{-1}$) and phenyl rings ($1\,604\text{ cm}^{-1}$, $1\,518\text{ cm}^{-1}$ and $1\,464\text{ cm}^{-1}$). The ^1H NMR spectrum of **1** (Table 1) revealed the presence of two sets of 1, 2, 4-trisubstituted aromatic signals [δ_{H} 6.52 (1H, d, $J=1.8\text{ Hz}$, H-2'), 6.53 (1H, d, $J=8.0\text{ Hz}$, H-5'), 6.41 (1H, dd, $J=8.0$, 1.8 Hz , H-6'); 6.60 (1H, d, $J=1.6\text{ Hz}$, H-2''), 6.55 (1H, d, $J=8.0\text{ Hz}$, H-5''), 6.50 (1H, dd, $J=8.0$, 1.6 Hz , H-6'')], two methine signals [δ_{H} 4.67 (1H, d, $J=8.0\text{ Hz}$, H-3); 2.83 (1H, m, H-2)], one oxygenated methylene signal [δ_{H} 3.84 (1H, dd, $J=10.5$, 5.8 Hz , H-1a), 3.71 (1H, dd, $J=10.5$, 6.9 Hz , H-1b)], in addition to two methoxy signals [δ_{H} 3.62, 3.61 (each 3H, s)]. In the ^{13}C NMR and DEPT spectra of **1**, seventeen carbon signals were observed, including twelve sp^2 aromatic carbon [δ_{C} 146.6×2 , 144.9, 144.5, 135.4, 132.0, 121.3, 119.2, 114.6, 114.4, 113.4, 111.2] arising from two benzene rings, three sp^3 carbons [δ_{C} 75.2, 63.3, 54.7], and two methoxy carbons [δ_{C} 55.5, 55.4]. On the basis of the HSQC and ^1H - ^1H COSY spectra of **1**, a spin system proton signals [H-3 (δ_{H} 4.67), H-2 (δ_{H} 2.83) and H-1a (δ_{H} 3.84), H-1b (δ_{H} 3.71)] was established. The results suggested the presence of propyl moiety in the structure of **1**. The propyl moiety was linked to the C-1' and C-1'' of benzene rings on the basis of the HMBC correlations of H-3/C-1' (δ_{C} 132.0), H-2/C-1', and H-3/C-1'' (δ_{C}

135.4), C-2'' (δ_{C} 111.2), C-6'' (δ_{C} 119.2) (Fig. 1). In the ROESY spectrum, the proton signals of two methoxy groups at δ_{H} 3.62 (3H, s) and 3.61 (3H, s) correlated with H-2' and H-2'', respectively, suggesting the two methoxy groups located at C-3' (δ_{C} 146.6) and C-3'' (δ_{C} 146.6). Because the optical rotation of compound **1** ($[\alpha]_{\text{D}}^{25.8} +20.0$, $c=0.9$, CH_3OH) was similar to those of (2*S*)-3, 3-diphenylpropane-1, 2-diol ($[\alpha]_{\text{D}} +48.0$, $c=1.0$, CH_3OH) (Gopishett *et al.*, 2011), suggesting that the absolute configuration of **1** at C-2 was *S*. Thus, compound **1** was identified as (2*S*)-3, 3-di-(4-hydroxy-3-methoxyphenyl)-propane-1, 2-diol.

The known compound shizukanolide E (**2**) was identified on the basis of reported physical NMR and ESIMS data (Li *et al.*, 2005). The previous phytochemical investigations on *Sarcandra glabra* were mainly focused on the EtOH extract, the type of new compound isolated from the water extract was different from that of EtOH extract. And the studies on the water extract of this plant made a little contributions to the qualities of the marketed products.

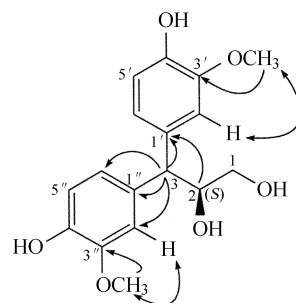


Fig. 1 Key HMBC (→) and ROESY (↔) correlations of **1**

Table 1 NMR data for compound **1** in $\text{DMSO}-d_6$ (400 MHz for ^1H)

position	δ_{H} (mult, J)	δ_{C} (mult)	position	δ_{H} (mult, J)	δ_{C} (mult)
1a	3.84 (dd, 1H, $J=10.5$, 5.8 Hz)	63.3 (t)	1''		135.4 (s)
1b	3.71 (dd, 1H, $J=10.5$, 6.9 Hz)		2''	6.60 (d, 1H, $J=1.6\text{ Hz}$)	111.2 (d)
2	2.83 (m, 1H)	54.7 (d)	3''		146.6 (s)
3	4.67 (d, 1H, $J=8.0\text{ Hz}$)	75.2 (d)	4''		144.9 (s)
1'		132.0 (s)	5''	6.55 (d, 1H, $J=8.0\text{ Hz}$)	114.6 (d)
2'	6.52 (d, 1H, $J=1.8\text{ Hz}$)	113.4 (d)	6''	6.50 (dd, 1H, $J=8.0$, 1.6 Hz)	119.2 (d)
3'		146.6 (s)	3'-OCH ₃	3.62 (s, 3H)	55.4 (q)
4'		144.5 (s)	3''-OCH ₃	3.61 (s, 3H)	55.5 (q)
5'	6.53 (d, 1H, $J=8.0\text{ Hz}$)	114.4 (d)			
6'	6.41 (dd, 1H, $J=8.0$, 1.8 Hz)	121.3 (d)			

Experimental

General experimental procedures UV spectra were measured on a JASCO V-550 UV/vis spectrophotometer. IR spectra were recorded on a JASCO FTIR-400 spectrometer. 1D and 2D NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C). ESI-MS data were recorded on a Finnigan LCQ Advantage MAX mass spectrometer. HR-ESI-MS data were determined by an Waters Synapt G2 MS mass spectrometer. HPLC was performed on a Gilson system with a 306 pump and a UV/vis-152 detector, using a reversed phase column (21.2×250 mm, 5 μm , Welch XB-C18) at 8 mL/min and monitored at 280 nm. Open column chromatography (CC) was performed using silica gel (200–300 mesh, Qingdao Marine Chemical Co. Ltd., Qingdao), ODS (50 μm , YMC), and Sephadex LH-20 (Pharmacia). Thin-layer chromatography (TLC) was performed using precoated silica gel plates (silica gel GF₂₅₄, 1 mm, Yantai).

Plant Material The plant material was generously provided by Guangzhou Jingxiutang Pharmaceutical Co. Ltd. (Guangzhou, China), and was identified as the whole plant of *Sarcandra glabra* by Professor Guang-xiong Zhou (College of Pharmacy, Jinan University). A voucher specimen (20070910) was maintained in Institute of Traditional Chinese Medicine & Natural Products, Jinan University, Guangzhou 510632 China.

Extraction and Isolation The whole dried plants (4.0 kg) of *S. glabra* were refluxed with water twice, for two hours each time. After evaporation of solvent in *vacuo*, the residue (446.4 g) was diluted with water. The filtrate was separated on macroporous adsorption resin Diaion HP20 using water and 30%, 50%, and 90% EtOH-H₂O in sequence to afford four fractions (parts A-D). Part C (42.6 g) was chromatographed over ODS column and eluted with MeOH-H₂O (9 : 1 to 0 : 1) to afford five fractions. Fraction 3 was further subjected to Sephadex LH-20 column chromatography using CHCl₃-MeOH

(1 : 1) as eluents and finally purified by prep. HPLC with MeOH-H₂O-HAc (40 : 60 : 0.1) to afford the compound **1** (2.0 mg). Fraction 4 was further subjected to silica gel column chromatography eluted with CHCl₃-MeOH (9 : 1) and finally purified by Sephadex LH-20 using CHCl₃-MeOH (1 : 1) to yield compound **2** (4.0 mg).

(2S)-3, 3-di-(4-hydroxy-3-methoxyphenyl)-propane-1, 2-diol (**1**): C₁₇H₂₀O₆, white amorphous powder. $[\alpha]_{\text{D}}^{25.8} +20.0$ (*c* 0.9, CH₃OH). IR (KBr) ν_{max} cm⁻¹: 3397, 2937, 1604, 1518, 1464, 1432, 1125, 821. UV (CH₃OH) λ_{max} (log ϵ): 211 (3.95), 228 sh (3.72), 280 (3.39) nm. ^1H NMR and ^{13}C NMR data see Table 1. Negative ESI-MS *m/z*: 319 [M-H]⁻, 639 [2M-H]⁻; HR-ESI-MS *m/z*: 319.1183 [M-H]⁻ (calcd for C₁₇H₁₉O₆, 319.1182).

Acknowledgments: We thank Jian-liang Geng, Tao Shi and Rong Ding for measuring the HR-ESI-MS and NMR data.

References:

- Gopishetty B, Gogoi S, Dutta AK, 2011. An improved asymmetric synthetic route to a novel triple uptake inhibitor antidepressant (2S, 4R, 5R)-2-benzhydryl-5-(4-methoxybenzyl) amino)-tetrahydro-2H-pyran-4-ol (D-142) [J]. *Tetrahedron: Asymmetry*, **22** (10): 1081–1086
- Hu XR, Yang JS, Xu XD, 2009. Three novel sesquiterpene glycosides of *Sarcandra glabra* [J]. *Chemical & Pharmaceutical Bulletin*, **57** (4): 418–420
- Huang SQ (黄胜强), Huang J (黄娟), Wang BL (王冰岚) *et al.*, 2010. Studies on chemical constituents of *Sarcandra glabra* [J]. *Chinese Traditional and Herbal Drugs* (中草药), **41** (2): 198–201
- Li CJ (李剑军), Zhang DM (张东明), Luo YM (罗永明), 2005. Studies on the chemical constituents from the roots of *Chloranthus henryi* [J]. *Acta Pharmaceutical Sinica* (药学报), **40** (6): 525–528
- Li Y, Zhang DM, Li JB *et al.*, 2006. Hepatoprotective sesquiterpene glycosides from *Sarcandra glabra* [J]. *Journal of Nature Products*, **69** (4): 616–620
- Takeda Y, Yamashita H, Matsumoto T *et al.*, 1993. Chloranthalactone F, A sesquiterpenoid from the leaves of *Chloranthus glaber* [J]. *Phytochemistry*, **33** (3): 713–715
- Tsui WY, Brown GD, 1996. Cycloodesmanolides from *Sarcandra glabra* [J]. *Phytochemistry*, **43** (4): 819–821